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# 1 **Liquid-liquid transition and critical point in sulfur**

2 Laura Henry<sup>1</sup>, Mohamed Mezouar<sup>1\*</sup>, Gaston Garbarino<sup>1</sup>, David Sifré<sup>1</sup>, Gunnar Weck<sup>2</sup> &  
3 Frederic Datchi<sup>3</sup>

4 <sup>1</sup>*European Synchrotron Radiation Facility (ESRF), 71, Avenue des Martyrs, Grenoble,*  
5 *France*

6 <sup>2</sup>*CEA, DAM, DIF, F-91297 Arpajon, France*

7 <sup>3</sup>*Institut de Minéralogie, de Physique des Milieux Condensés et de Cosmochimie*  
8 *(IMPMC), Sorbonne Université, CNRS UMR 7590, MNHN, 4 place Jussieu, F-75005*  
9 *Paris, France*

10 **A liquid-liquid transition (LLT) is a peculiar phenomenon in which a single-**  
11 **component liquid transforms into another one via a first-order phase transition. Due**  
12 **to their counterintuitive nature, LLTs have intrigued scientists for several years and**  
13 **changed our perception of the liquid state. Such LLTs have been predicted from**  
14 **computer simulations of water<sup>1,2</sup>, silicon<sup>3</sup>, carbon dioxide<sup>4</sup>, carbon<sup>5</sup>, hydrogen<sup>6</sup> and**  
15 **nitrogen<sup>7</sup>. Experimental evidence has been mostly found in supercooled, i.e.**  
16 **metastable, liquids such as Y<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> mixtures<sup>8</sup>, water<sup>9</sup> and other molecular**  
17 **liquids<sup>10,11,12</sup>, but the LLT in supercooled liquids often occurs simultaneously with**  
18 **crystallization, making it hard to separate the two phenomena<sup>13</sup>. A liquid-liquid**  
19 **critical point (LLCP), similar to the gas-liquid critical point, has been predicted at**  
20 **the end of the LLT line in some cases, but so far never experimentally observed for**  
21 **any materials. This putative LLCP has for instance been invoked in the case of water**  
22 **to understand its thermodynamic anomalies<sup>1</sup>. Here we report combined *in-situ***  
23 **density measurements, x-ray diffraction and Raman scattering that provide direct**  
24 **evidence for a first-order liquid-liquid transition and a liquid-liquid critical point in**  
25 **sulfur. The transformation manifests itself by a sharp density jump between the low**

26 **and high density liquids, and distinct features in the pair distribution function. A**  
27 **non-monotonic variation of the density jump with temperature is observed, which**  
28 **first increases on moving away from the critical point and then decreases. This**  
29 **behavior is linked to competing effects of density and entropy in driving the**  
30 **transition.**

31 The pressure (P)-temperature (T) phase diagram of sulfur exhibits important  
32 similarities with that of phosphorus which is to date the only element for which a direct  
33 *in-situ* observation of a LLT has been unambiguously evidenced<sup>14,15,16</sup>. The stable sulfur  
34 solids at room P,  $\alpha$ - and  $\beta$ -sulfur<sup>17,18</sup>, consist of S<sub>8</sub> molecules, while at high P-T, the stable  
35 polymorph is a polymeric solid composed of helical chains<sup>19</sup>. At room P the molecular  
36 character is conserved in the liquid upon melting at 388 K and up to 432 K where the so-  
37 called “lambda transition” ( $\lambda$ -T) occurs<sup>20</sup>. The  $\lambda$ -T has been described as a “living”  
38 polymerization transition<sup>21</sup>, reversible and incomplete (the polymer content reaches a  
39 maximum of ~60% at the boiling point, T=718 K), where a fraction of the S<sub>8</sub> cyclic  
40 molecules open up and coalesce into long polymeric chains or rings. It is associated with  
41 a large increase in viscosity and an anomalous but not discontinuous density variation<sup>20,22</sup>.  
42 For P above 5 GPa and T above 1000 K, several P-T domains with different thermal and  
43 electrical properties have been proposed in liquid sulfur<sup>23</sup>. An experimental study<sup>24</sup>  
44 suggested the existence above 6 GPa of a purely polymeric liquid composed of long  
45 chains below 1000 K, which split to shorter chains at higher temperature. *Ab-initio*  
46 molecular dynamics simulations<sup>25</sup> reproduced this chain breakage in the compressed  
47 liquid but found no discontinuous change of density associated to this process. So far, no  
48 *in-situ* structural or vibrational studies have been conducted in the pressure region below  
49 3 GPa in the mixed molecular-polymeric liquid.

50 We performed *in-situ* x-ray absorption, x-ray diffraction and Raman scattering at  
51 the beamline ID27 of the European Synchrotron Radiation Facility (ESRF)<sup>26</sup> to probe the  
52 density, structure and dynamics evolution of liquid sulfur in the P-T domain 0-3 GPa,  
53 300-1100 K (see Supplementary Information S1-S3 for methods). The P-T paths are  
54 represented in the experimental phase diagram of sulfur in Fig. 1.

55

## 56 **Figure 1**

57 Density measurements were obtained in the Paris-Edinburgh press along eight  
58 isothermal (P1 to P8 in Fig. 1) and two isobaric pathways (P9 and P10). The accuracy of  
59 the density measured by this method is of the order of 1% (Supplementary Information  
60 S1). XRD patterns of the sample were also collected at each P-T point to confirm that the  
61 sample was fully molten. As shown in Fig. 2a, along isothermal pathways P1-P5 below  
62 1000 K, we systematically observed a discontinuous jump in density over a very narrow  
63 pressure domain of  $\sim 0.07$  GPa, strongly suggesting the existence of a first-order phase  
64 transition between a low (LDL) and a high density liquid (HDL). Discontinuous density  
65 shifts were also observed upon varying the temperature at constant load along pathways  
66 P9-P10 (Supplementary Figure S9). These density jumps were accompanied by sudden  
67 changes in the structure factor  $S(Q)$  of the sulfur melt, as shown in Fig. 2b. This is  
68 particularly apparent on the width and position of the first diffraction peak which abruptly  
69 change at the transition. The density variation estimated from the measured  $S(Q)$  using  
70 the methodology of Ref. [27] (see Supplementary Information S3) very well compares  
71 with that derived from the x-ray absorption measurements (see inset of Fig. 2c), giving  
72 an independent confirmation of the discontinuous density jump at the transition.

73 Fig. 2c presents x-ray radiographic images taken along a compression pathway at  
74 980 K and pressures between 1.6 and 2.5 GPa. These images show that below (panel *i*)  
75 and above (panel *iv*) the transition, the sample is homogeneous, while at the transition an  
76 interface separating a “bubble” of HDL from the surrounding LDL appears (panels *ii* and  
77 *iii*). As seen in the Supplementary video 1, the HDL bubble grows as the load is increased  
78 until the sample is fully in the HDL phase. These observations provide a compelling  
79 evidence of a coexistence of the LDL and HDL phases at the transition, and together with  
80 the density and structure factor measurements, confirm the first-order nature of the liquid-  
81 liquid transition.

82 At 1090 K and 1100 K (pathways P7 and P8 in Fig. 1), we did not observe, within  
83 uncertainties, any discontinuous shift of the density as a function of pressure thus  
84 indicating the presence of a liquid-liquid critical point (LLCP). The LLCP was likely  
85 crossed along the pathway P6 at  $\sim 2.15$  GPa and 1035 K (indicated by a star in Fig. 2a)  
86 where the density measurements show clear anomalies (see Supplementary Information  
87 S2), while at lower and higher pressures along this isotherm, the density appears to  
88 continuously vary with pressure. As shown in Fig. 2d, we observe a non-monotonic  
89 evolution of the density discontinuity with temperature: starting from zero at the LLCP,  
90 it first increases to reach a maximum of  $\sim 7.5\%$  at about 750 K and then decreases.

## 91 **Figure 2**

92 Fig. 3a shows the pair distribution function (PDF)  $g(r)$  obtained by Fourier  
93 transform of the measured  $S(Q)$  at 5 selected points along the P8 pathway: A, B and C  
94 are in the LDL domain, while D and E are in the HDL domain, close to the LDL-HDL  
95 transition line (see Fig. 1). The LDL PDF at point A (0.11 GPa, 428 K) is very similar to  
96 those reported for the ambient-pressure molecular liquid below the lambda transition<sup>28,29</sup>.

97 It displays three well-defined peaks at 2.05, 3.39(2) and 4.45(2) Å, in very good  
98 agreement with the previous cited works. As shown in the latter, the third peak is a  
99 fingerprint of the S<sub>8</sub> molecule since it occurs at the average distance of the third and fourth  
100 neighbors in a S<sub>8</sub> ring, as deduced from the structure of the molecular α-sulfur crystal.  
101 When the temperature is increased in the LDL domain above the lambda transition (points  
102 B at 0.17 GPa-442 K, and C at 0.36 GPa-487 K), the observed evolution is also very  
103 similar to that described in the literature for the ambient-pressure liquid<sup>28</sup>. Namely, the  
104 positions and intensities of the first and second-neighbor peaks are weakly affected,  
105 whereas the third peak strongly reduces in intensity and becomes bi-modal. These  
106 changes in the third/fourth neighbor distribution are a signature of the rapid increase of  
107 polymer content and associated reduction of the S<sub>8</sub> content above the lambda transition.  
108 Indeed, the peak at 4.45 Å, characteristic of S<sub>8</sub> molecules, reduces in intensity and a new  
109 component at 4 Å appears and grows with temperature, originating from the formation of  
110 long polymeric chains or rings. The similarities between the present PDF in the region  
111 from 4 to 5 Å and those reported by Bellissent et al.<sup>28</sup> from ambient-pressure neutron  
112 diffraction can be appreciated from the comparison of the inset of Fig. 3a and Fig. 3b. We  
113 note however that the new component in the ambient pressure PDF appears at a larger  
114 distance, around 4.2 Å, which is likely due to the lower density of the ambient pressure  
115 liquid.

### 116 **Figure 3**

117

118 We now come to the structural modifications in the PDF across the LDL-HDL  
119 transition. As seen in Fig. 3c and S15, no change, within uncertainties, occurs on the first  
120 and second peak positions, showing that the S-S bond length and the <S-S-S> angle are

121 the same as in the LDL. The most important modifications occur again in the third/fourth-  
122 neighbour distributions. The bi-modal shape of the third peak is maintained but the  
123 component at 4.45 Å is even more reduced, and the component located at 4 Å in the LDL  
124 undergoes a sudden shift in position to 4.15 Å in the HDL. This shows that the local order  
125 in the liquid changes at the transition, and further, suggests that the polymer content in  
126 the HDL is larger than in the LDL. The latter point is confirmed by the comparison of the  
127 Raman spectra measured in the LDL and HDL shown in Fig. 3d. In the HDL domain, we  
128 observe an intensity increase of the stretching mode at  $460\text{ cm}^{-1}$  assigned to the polymeric  
129 chains<sup>30</sup>, concomitant with a drop of the molecular bending mode at  $152\text{ cm}^{-1}$  and  
130 breathing mode at  $220\text{ cm}^{-1}$  of the  $S_8$  molecule, attesting that the latter are residual in the  
131 HDL region.

132 This work thus demonstrates that sulfur undergoes a first-order phase transition  
133 between two thermodynamically stable liquids, with clear experimental evidence of a  
134 sharp density increase and structural modifications. We stress that this LLT is distinct  
135 from the long-known lambda transition, which is associated to second-order like changes  
136 in density<sup>20,22</sup> and heat-capacity<sup>31</sup>. Furthermore, the lambda transition temperature slowly  
137 decrease with pressure<sup>32</sup> whereas for the present LLT, the transition temperature increases  
138 with pressure (see also Supplementary Information S4). By virtue of the Clapeyron  
139 equation, and since a positive jump of density occurs at the transition, this tells us that the  
140 entropy of the HDL is smaller than that of the LDL, which contrasts with the entropy  
141 increase in the LDL at the lambda transition<sup>33</sup>. The entropy reduction across the LLT may  
142 be due in part to the increase in polymer content revealed by present experiments, and  
143 associated reduction in the mixing entropy. But the observed changes in the PDF also  
144 indicate that the local conformation of neighbor polymeric units is modified, certainly to

145 a more compact arrangement imposed by the density increase, leading to a reduction in  
146 the conformation entropy as well.

147 The shape of the transition line and the presence of a critical point make this LLT  
148 in sulfur strongly resemble the well-known liquid-gas transition (LGT). However, there  
149 is an important difference, which is the non-monotonic variation of the density jump with  
150 temperature of the LLT, which first increases from zero as the temperature is decreased  
151 from the LLCP and then decreases, contrasting with the monotonic increase of density  
152 along the LGT transition. Such a behavior was recently predicted by AIMD calculations  
153 along the LLT line of phosphorus<sup>34</sup>, from which the authors suggested that the order  
154 parameter describing the LLT contains contributions from both the density and entropy,  
155 and that at least at low temperatures, entropy governs the transition rather than density.  
156 This is at odds with the LGT where density is the sole order parameter. A two-order  
157 parameters model including density, on one hand, and a bond-order parameter describing  
158 locally favoured structures, on the other hand, was also proposed by Murata and Tanaka<sup>13</sup>  
159 to explain the existence of LLTs. The putative LLT in water has also been described as  
160 entropy-driven based on a model where water is considered as an “athermal solution” of  
161 two molecular structures with different entropies and densities<sup>35</sup>. We note however that  
162 the present LLT in sulfur is different from that in water and phosphorus in the sense that  
163 the transition line has a positive slope in sulfur but a negative one in water and  
164 phosphorus. This may signal that sulfur belongs to a different class of LLT.

165 This work also provides the first, to the best of our knowledge, experimental  
166 evidence for a critical point terminating the line of a LLT. Such a LLCP was proposed in  
167 phosphorus at about 3500 K – 0.02 GPa<sup>34</sup>, conditions which have not yet been achieved  
168 by experiment. In supercooled liquid silicon, classical empirical calculations have



169 predicted a LLCPP at negative pressures (-0.6 GPa, 1120 K)<sup>36</sup> but *ab-initio* calculations  
170 recently determined that the HDL and HDL-vapor spinodals form a continuous reentrant  
171 curve, making supercooled Si a critical point free system<sup>37</sup>. In water, the existence of a  
172 LLCPP has been conjectured by Poole in 1992 et al.<sup>1</sup> to explain the many anomalies in the  
173 thermodynamic properties such as the heat capacity, compressibility and thermal  
174 expansion coefficients, and evidence for this LLCPP has been strongly searched for and  
175 debated ever since. The experimental observation of this hypothetical LLCPP in water may  
176 well never be possible as it is located in the “no man’s land”, i.e. the P-T domain below  
177 the homogeneous nucleation temperature. Finally, a LLCPP has also been predicted in  
178 simple molecular systems, such as H<sub>2</sub><sup>6</sup> and N<sub>2</sub><sup>7</sup> but their experimental observation remain  
179 extremely challenging. The LLCPP in sulfur, being in a P-T range easily accessible by  
180 experiment, provides a unique opportunity for the study of critical phenomena associated  
181 to LLTs. We thus expect that the present work will spark a new interest in liquid-liquid  
182 transitions that will provide a solid basis for understanding the principles that govern  
183 LLTs in general. Future works should also focus on deciphering the microscopic  
184 processes at the origin of the LLT in sulfur.

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## 297 **Figure Legends**

298 **Fig. 1. Phase diagram of sulfur around the liquid-liquid transition.** P1 to P8:  
 299 isothermal pathways followed during the density measurements presented in Fig. 2. P1,  
 300 P2, P4 to P7 were made on compression while P3 (diamond symbols) and P7 (open black  
 301 **circles**) were made on decompression. For clarity, P7 and P8 are shown up to 3 GPa only.  
 302 P9 and P10 are isobaric pathways followed during the density measurements presented  
 303 in Fig. S9 (Supplementary Information S1). The letters A, B, C, D, E (blue filled triangles)  
 304 along path P11 indicate the P, T conditions of the selected XRD data in Fig. 3. I, II and  
 305 III are the P,T points of the Raman spectra presented in Fig. 3. The black dashed line is  
 306 the transition line between the low density liquid (LDL) domain (in yellow) and the high  
 307 density liquid (HDL) domain (in pink) that terminates at the critical point **C<sub>p</sub>** (black solid  
 308 circle).

309 **Fig. 2. First-order liquid-liquid transition in sulfur. a.** Relative pressure variation of  
 310 the liquid density  $\rho/\rho_0$  ( $\rho_0$ : density of the lowest pressure point for each isotherm)  
 311 collected along seven isothermal pathways (P1, P2 and P4 to P8 in Fig. 1). For clarity,  
 312 the density jump obtained on decompression along P3 and along the isothermal paths P9  
 313 and P10 are presented in the Extended Data Fig. 1 and 3. Main panel: at T below 1030 K,  
 314 a clear density jump is observed along all the isothermal paths. At ~1035 K, a density  
 315 anomaly is detected in the vicinity of the LLCP (see Extended Data Fig. 4). Above the  
 316 LLCP (inset panel), a continuous variation of the density is observed. **b.** Structure factors  
 317  $S(Q)$  of liquid sulfur collected along the isothermal path P2 (T=650 K). The red arrow  
 318 emphasizes the shift of the first peak position of  $S(Q)$  at the LDL-HDL transition. The  
 319  $S(Q)$ 's collected on decompression at 740 K are shown in the Extended Data Fig. 2. The  
 320 variation of the density calculated from the associated Pair Distribution Function (PDF)  
 321 (black filled squares) is presented in the inset panel together with the one obtained from  
 322 the direct density measurements (red empty squares). **c.** X-ray radiography of liquid sulfur  
 323 across the LDL-HDL transition line at T=980 K and pressures between 1.6 and 2.5 GPa.

324 *i*: Pure LDL, *ii and iii*: LDL-HDL coexistence, *iv*: Pure HDL. The yellow arrow indicates  
 325 the LDL-HDL boundary. **d**. Temperature evolution of the density jump. The black and  
 326 blue symbols correspond to the isothermal pathways (P1 to P8) and, the red symbols to  
 327 the isobaric (P9 and P10) pathways. A maximum of 7.5 % is located at ~750 K.

328 **Fig. 3. Local order in the low- and high-density liquid sulfur.** **a**. The main panel  
 329 presents the pair distribution function  $g(r)$  of liquid sulfur at selected pressure and  
 330 temperature conditions along path P11 of Fig. 1. The letters A to E in parentheses refers  
 331 to the P,T conditions in Fig. 1 at which the measurements were performed. The curves  
 332 are vertically offset by 0.3 for clarity. The inset shows an enlargement of the PDF in the  
 333 region from 0.4 to 0.5 nm which contains contributions from third and fourth neighbours.  
 334 **b** shows an enlargement of the third peak of  $G(r)$  from the ambient-pressure neutron data  
 335 of Ref. 28 at 423 K, 473 K and 573 K (the curves were digitized from Fig. 2 of Ref. 28).  
 336 **c** presents the position of the second, third and fourth neighbours as a function of pressure,  
 337 as deduced from the peak positions of the PDF along the path P11. Panel **d** shows selected  
 338 Raman spectra of liquid sulfur collected at the P,T points I,II and III of Fig.1. I: LDL  
 339 below the  $\lambda$ -T. II: LDL above the  $\lambda$ -T. III: HDL.

### 340 **Extended Data Figure Legends**

341 **Extended Data Fig 1. Density discontinuity at 740 K.** Raw datasets of isothermal x-  
 342 ray absorption profiles  $I/I_0$  collected on decompression at 740 K. The black arrow  
 343 indicates the density jump. B. Resulting isothermal density curve of sulfur in red and  
 344 density variation of NaCl pressure standard in blue.

345 **Extended Data Fig 2. Structure factors  $S(Q)$  of liquid sulfur collected on**  
 346 **decompression along the isothermal path  $T=740$  K.** The black arrow emphasizes the  
 347 shift of the first peak position of  $S(Q)$  at the HDL-LDL transition. The variation of the  
 348 density calculated from the associated Pair Distribution Function (PDF) (black filled

349 squares) is presented in the inset panel together with the one obtained from the direct  
350 density measurements (red empty squares).

351 **Extended data Fig 3. Isothermal density discontinuity.** Density of liquid sulfur as a  
352 function of temperature along isobaric paths P9 at 0.4 GPa (left panel) and P10 at 1.3 GPa  
353 (right panel).

354 **Extended Data Fig 4. Liquid-liquid critical point in sulfur. Panels a and b:** X-ray  
355 absorption profiles  $I/I_0$  in the horizontal and vertical directions in the vicinity of the  
356 critical point. **Panels c and d:** Horizontal x-ray absorption profiles at temperatures  
357 below (950 K) and above (1090K) the critical point. The red arrow in panel **c** indicates  
358 the  $I/I_0$  discontinuity at the liquid-liquid transition. No  $I/I_0$  discontinuity is observed at  
359 temperature above the critical point (panel **d**).

360

### 361 **Methods**

362 Methods are available in the Supplementary Information at <https://XXX>

363

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### 369 **Author contributions**

370 The original idea was defined by MM. The experiments were performed by LH, GG,  
371 DS and MM with equal contributions. The data were analysed and the figures produced



372 by LH with contributions from all the co-authors. The manuscript was written by MM  
373 and FD with contributions from all the co-authors.

374 Correspondence and requests for materials should be addressed to M. M.  
375 ([mezouar@esrf.fr](mailto:mezouar@esrf.fr)).

### 376 **Data Availability**

377 Tables containing the data points for all the main and extended data figures are provided  
378 as Excel files. The data that support the findings of this study are available from the  
379 corresponding author upon request.

### 380 **Competing interests**

381 The authors declare no competing interests.





